PB-228 775

INDUSTRIAL WASTE SURVEY REPORT. A STUDY OF THE CHARACTERISTICS OF LIQUID WASTES FROM A BY-PRODUCT COKE PLANT, MAY 14 TO JUNE 21, 1950

Stanley G. Monroe

Environmental Health Center
Cincinnati, Ohio

1974

DISTRIBUTED BY:

NTIS

National Technical Information Service
U. S. DEPARTMENT OF COMMERCE
5285 Port Royal Road, Springfield Va. 22151

PB 228 775

1.

Industrial Waste Survey Report

A Study of the Characteristics of Liquid Wastes from a By-Product Coke Plant

May 14 to June 21, 1950

By

Stanley G. Monroe
Sanitary Engineer

FEDERAL SECURITY AGENCY
Public Health Service
Environmental Health Center
Cincinnati, Ohio

60

Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
U S Department of Commerce
Springfield VA 22151

TABLE OF CONTENTS

	Page
ABSTRACT	1
GENERAL INFORMATION	4
1. Organization of Survey	4
2. Dates	4
3. Purpose	4
4. Production	4
5. Water Supply	5
6. Waste Disposal	5
7. Sanitary Sewage	5
DISCUSSION OF PROCESS	6
8. Carbonization	6
9. Coke Quenching	7
10. Gas Collection	9
11. Primary Coolers	9
12. Exhausters and Precipitators	10
13. Phenol Recovery	10
14. Ammonia Recovery	13
15. Saturators	13
16. Pyridine Recovery	14
17. Final Coolers	14
18. Benzol Washers	16
19. Light Oils and Their By-Products	16
20. Tar Disposal	17

SURVEY PROCEDURES 18

21. Sample Collection 18

22. Flow Measurements 19

23. Laboratory Analyses 20

EXPLANATION OF LABORATORY ANALYSES 20

24. Phenols 20

25. Cyanides 21

26. Sulphur Compounds 21

27. Ammonia 21

28. pH 22

29. Alkalinity 22

30. Chlorides 22

DISCUSSION OF RESULTS 23

31. Discharge 33

32. Ammonia Still Effluent 34

33. Intercepting Sumps 35

34. Quench Water 36

SUMMARY 36

35. Quality of Liquid Wastes Discharged 36

36. Quantity of Significant Constituents 37

37. Unit Values 37

38. Average Yield 38

SPECIAL STUDIES 38

39. Dephenolizing Tower 38

40. Final Cooler System 40

REFERENCES 47

APPENDIX 48

1. Procedures for Cyanide Analysis 49

2. Determination of Phenols (Bromination Procedure) 51

3. Determination of Phenols (Gibbs Method) 52

4. Thiocyanates in Gas Ammonia Liquor 53

5. Procedure for Ammonia Analysis 54

LIST OF TABLES

Table 1 - Production Data 25

Table 2 - Summary of Laboratory Analyses 27-30

Table 3 - Average Concentration of Constituents 31

Table 4 - Gross Quantities of Significant Constituents Discharged Daily 32

Table 5 - Net Quantities of Significant Constituents Discharged Daily 32

Table 6 - Dephenolizing Plant - % Phenol Removed 39

Table 7 - Concentration of Significant Constituents in Final Cooler System 42

Table 8 - Quantities of Significant Constituents in Final Cooler System 43

Table 9 - Average Qyantities of Significant Constituents in Final Cooler System 44

LIST OF FIGURES

Fig. 1 - Flow Diagram 8

Fig. 2 - Dephenolizing Unit 12

Fig. 3 - Pyridine Recovery System 15

ABSTRACT

This study was made in connection with the program of industrial waste studies being conducted by the Public Health Service in cooperation with State Health Departments and other agencies concerned. The primary purpose is to determine the sources, quantities, and characteristics of wastes produced together with a study of the processes or conditions that materially affect the quantity and characteristics of these wastes. A study was made of the discharges from the principal waste producing operations of the plant. Special studies were made on the dephenolizing unit which employs the benzol extraction process, and also on the gas final cooler recirculating system.

This plant operates 385 ovens primarily for the production of metallurgical coke. During the period of the study an average of 6,828 tons of coal were carbonized and 5,329 tons of coke produced daily. Gas produced in the coking process is utilized in the plant.

During this period the plant discharged 91.3 lbs. of phenol daily. The ammonia still effluent contained 47.8 lbs., the benzol plant 38.3 lbs. and the coke quench water discharge 5.2 lbs. A total of 31.2 lbs. of cyanides were discharged of which 18.7 lbs. were contained in the ammonia still effluent and 12.5 lbs. in the discharge from the benzol plant.

Studies on the dephenolizing plant indicated a 90.9% removal of phenols from the weak ammonia liquor by this unit. A maximum removal of 93.1% was obtained during the period of study.

The study on the final cooler recirculation system was made to determine to what extent cyanides may be released to the atmosphere in the exhaust air from the Marley cooling tower. The analyses made indicated that an average of 656 lbs. were discharged daily through the exhaust stacks to the

atmosphere as compared to 31.2 lbs. from other plant units discharged in liquid wastes to the sewers. The phenols contained in the Marley exhaust vapors discharged to the atmosphere amounted to 12 lbs. per 24 hours during the period of the study.

GENERAL INFORMATION

1. Organization of Survey

This survey was conducted by the Environmental Health Center, U. S. Public Health Service, in cooperation with the plant officials. Preliminary conferences were held between representatives of both organizations and the Ohio State Department of Health regarding the scope and objectives of the survey. An agreement was reached relative to the scope of study that would be undertaken, and authority was granted the Public Health Service to carry on the study in accordance with this agreement.

2. Dates

The field work was conducted during the period from May 14, 1950 to June 21, 1950.

3. Purpose

The purpose of this study was to determine the quantities and characteristics of process wastes resulting from the operation of a by-product coke plant. It is expected that the information obtained will serve as an aid in determining the principal factors affecting the characteristics and quantities of by-product coke plant wastes. The primary objective is to obtain information suitable for the preparation of an industrial waste guide for by-product coke plants.

4. Production

The average daily production of coke and by-products during the period of the survey was reported as follows:

Coke (2.5% moisture basis)	- -	5,329 tons
Ammonia sulfate	- -	58.71 tons
Tar	- -	33,674 gallons
Gas	- -	78.85 mil. cu. ft.
Light Oil	- -	17,841 gallons

5. Water Supply

Water used in the coke plant is drawn from the municipal system for drinking, sanitary purposes, etc. River water is used in the main coke plant operation processes.

6. Waste Disposal

All process wastes from the coke plant are discharged to the main outfall sewer carrying the wastes from the steel mill operations. This outfall line in turn discharges direct to a river.

The principal sources of water originating in the coke plant that contain significant waste constituents are the ammonia still effluent and the discharge from the benzol plant processes. The benzol plant wastes are discharged through two intercepting sumps. The main intercepting sump (No. 1 sump) receives the major part of the wastes such as the oil decanter wastes, caustic wastes from agitators, spills and floor washes, etc. The discharge through the second sump (No. 2 sump) consists of cooling water discharged from the wash oil cooling coils (indirect cooling system). This discharge does not ordinarily contain any significant quantities of waste constituents except when leaks or breaks may occur in the wash oil coils.

7. Sanitary Sewage

Sanitary sewage from the coke plant is discharged to the above-mentioned outfall sewer along with the process wastes.

DISCUSSION OF PROCESS

High temperature carbonization of coal is the process used at this plant for the production of metallurgical coke. Practically the entire production of coke from this plant is used for metallurgical purposes. The principal products recovered in the process are tar, ammonium sulfate, pyridine, naphthalene and benzol products. The general operation of the various steps in the process are outlined below. Figure 1 is a general overall flow diagram for the entire plant.

8. Carbonization

The coke plant utilizes the Koppers and Wilputte types of regenerative coke ovens. These types of ovens are provided with facilities for temperature control through regulation of the fuel gas, air supply, and draft through the vertical and horizontal flues. The Koppers ovens are the "gun flue" type in which riser pipes from the main fuel gas main carry the gas to the horizontal distribution flues constructed of silica brick and lying under the vertical flues. The Wilputte ovens are provided with the underjet system for distributing fuel gas to the flame flues. Coke oven gas and preheated air are used for fuel in the operation of the ovens at this plant.

The types, dimensions, etc., of the ovens are as follows:

Batteries B, C, D, and E: 52 ovens each; Koppers type; placed in operation 1918; width tapering from 16 1/4" to 20 1/4", length 40'-0", height 10'-0"; capacity 500 cu. ft. and approximately 9 tons coke produced per charge; coke oven gas used for fuel.

Batteries J, K, and L: 59 ovens each; Wilputte type; placed in operation 1947; width tapering from 17" to 21", length 39'-4", height 10'-0"; capacity 555 cu.ft. and approximately 10 tons coke produced per charge; coke oven gas used for fuel.

A mixture of coke oven gas and pre-heated air is used for fuel in both the Koppers and Wilputte ovens. Volatile materials produced in the carbonization of the crushed coal charge are removed through one takeoff stack

from each Koppers oven, and through two takeoff stacks on each Wilputte oven. In the Koppers ovens one half of the flues in the oven wall are used as flame flues for combustion of the incoming fuel gases. The products of combustion pass to a horizontal flue along the top of oven wall and then through the downflow flues and brick checkerwork in the other half of the oven wall. This operation is reversed every one-half hour. In the Wilputte oven the horizontal combustion gas flue has a division wall at the center of oven wall. On each side of division wall one-half the vertical flues are used as flame flues while the other half serve as downflow flues. The flow through the vertical flues is periodically reversed at one-half hour intervals.

The coking time is 15 hrs., 36 min. and 17 hrs., 14 min. in the Koppers and Wilputte ovens, respectively. The following temperatures are maintained during the coking period: flues -2500° F.; oven walls -2000° F.; coke pushed -1900° F.

During the period of this study the coal blend used for carbonization consisted of 50% Pocahontas and 50% high volatile coals. The volatile matter in the Pocahontas coal averaged 17 to 18 per cent while the high volatile coal averaged 30 to 33 per cent. During the period of study the coal blend analyses averaged as follows: 4.95% moisture; 25.73% volatile matter; 68.09% fixed carbon; 6.19% ash; and 0.69% sulfur.

9. Coke Quenching

After carbonization is complete the hot coke is removed from oven by means of a mechanical pusher or ram to a quench car and taken to one of four quench stations. The amount of quench water used should be just sufficient to quench without leaving any excess water in the coke. Two quench stations are used for quenching coke from the Koppers ovens and two are used for coke from the Wilputte ovens. The runoff or drainage from the quenching operation

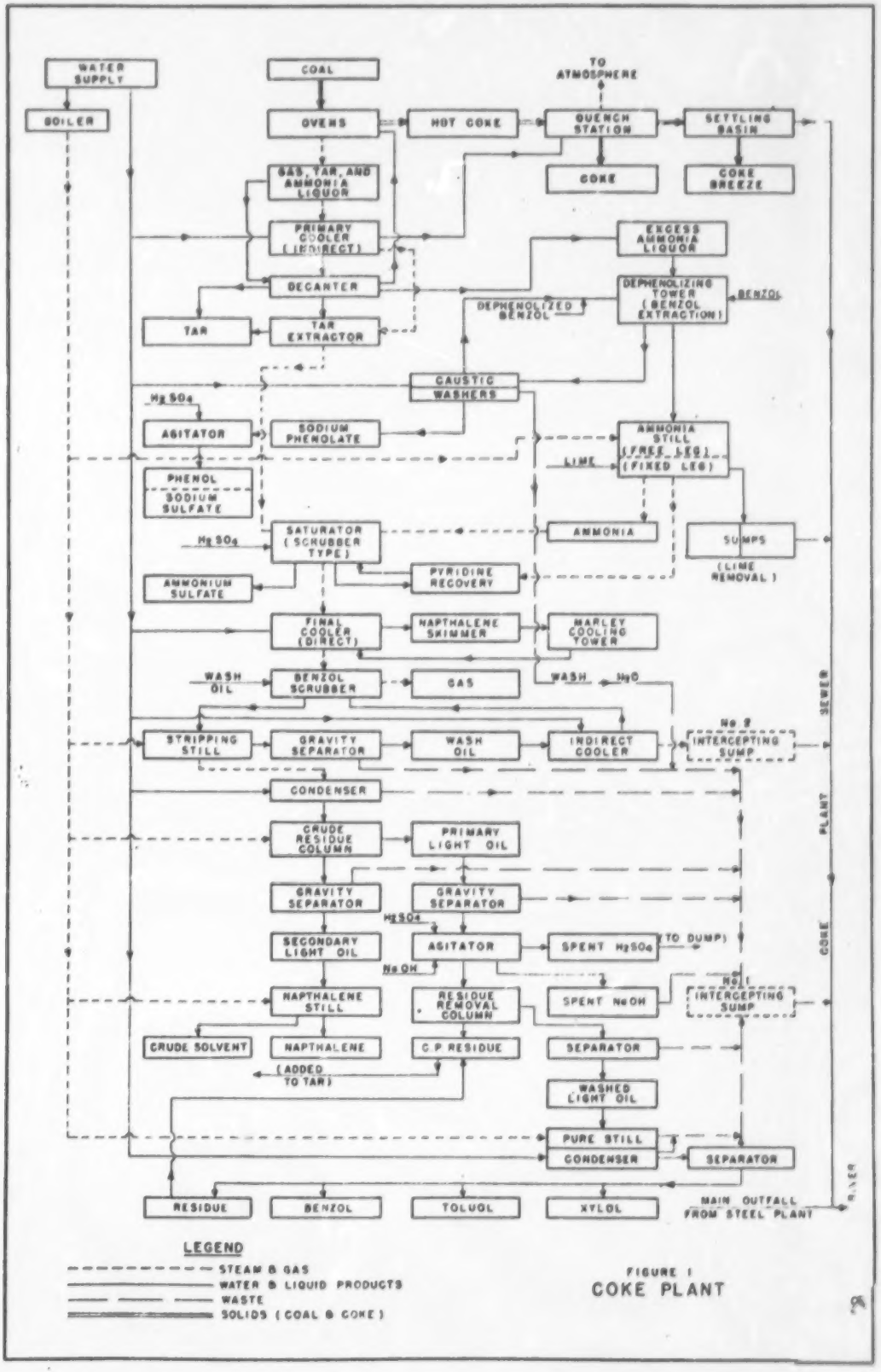
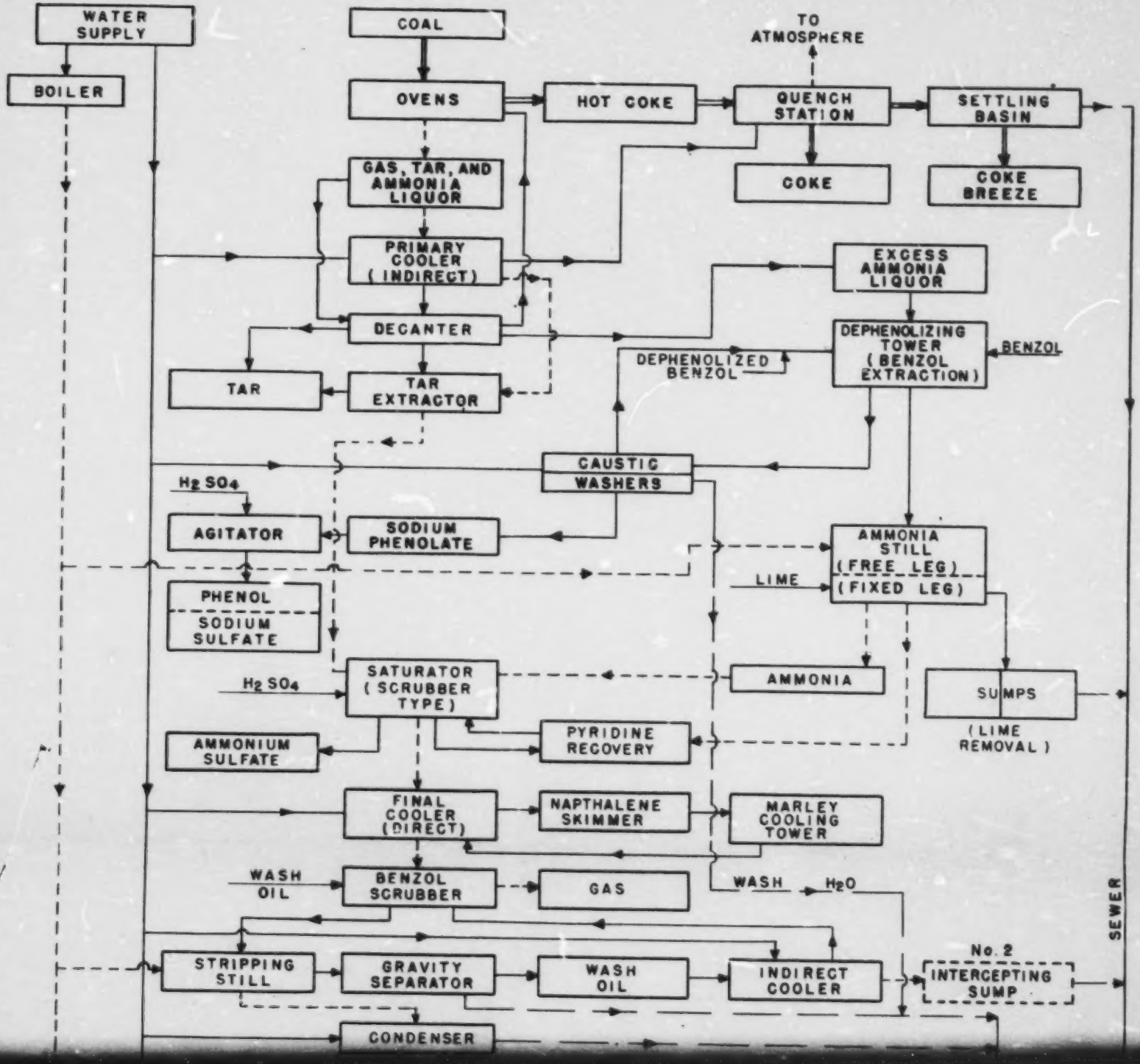


FIGURE 1
COKE PLANT


WATER SUPPLY
BOILER
COAL
OVENS
HOT COKE
TO ATMOSPHERE
QUENCH STATION
SETTLING BASIN
COKE
COKE BREEZE
GAS, TAR, AND AMMONIA LIQUOR
PRIMARY COOLER (INDIRECT)
EXCESS AMMONIA LIQUOR
DECANTER
DEPHENOLIZING TOWER (BENZOL EXTRACTION)
BENZOL
DEPHENOLIZED BENZOL
TAR
TAR EXTRACTOR
CAUSTIC WASHERS
H_2SO_4
AGITATOR
SODIUM PHENOLATE
AMMONIA STILL (FREE LEG) (FIXED LEG)
LIME
PHENOL
SODIUM SULFATE
SATURATOR (SCRUBBER TYPE)
AMMONIA
SUMPS
(LIME REMOVAL)
H_2SO_4
AMMONIUM SULFATE
PYRIDINE RECOVERY
FINAL COOLER (DIRECT)
NAPTHALENE SKIMMER
MARLEY COOLING TOWER
WASH OIL
BENZOL SCRUBBER
GAS
WASH
H_2O
SEWER
STRIPPING STILL
GRAVITY SEPARATOR
WASH OIL
INDIRECT COOLER
No. 2 INTERCEPTING SUMP
CONDENSER

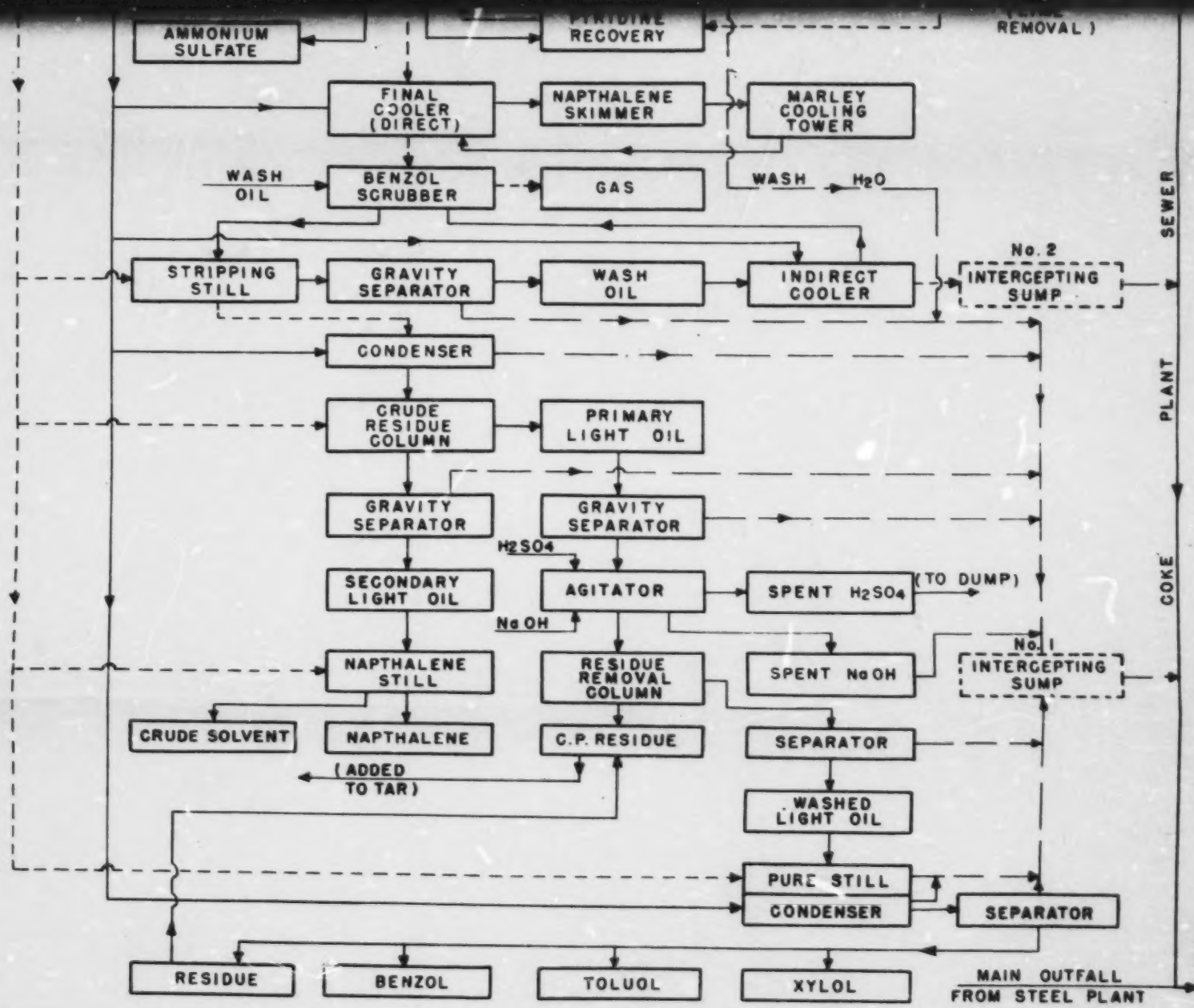


FIGURE 1
COKE PLANT

flows to a settling basin where the coke breeze is settled out and the supernatant water discharged to the sewer.

Approximately 5,500 gallons of water are used for each quench. Under normal operation there are about 558 quenches during each 24 hours or a total of 3,069,000 gallons of quench water used. It was estimated that approximately 75% of the total quench water used actually is discharged to the sewers. The other 25% is lost through evaporation and retention in the coke. On this basis about 2,300,000 gallons of quench water are discharged per day to the sewers from the four quench stations.

10. Gas Collection

Volatile material and gases produced in the carbonization of the coal pass through a take-off pipe at the top of each individual oven and connect into a collector main. A slight pressure is maintained in the ovens over and above the pressures in the collector main. When the differential reaches a certain point a butterfly valve permits the passage of gases from the oven to the collector main. As the gases and volatile materials enter the collector main they are sprayed with weak ammonia flushing liquor in order to cool the gases and absorb the ammonium salts and a portion of the free ammonia. This flushing liquor also carries away the tar, pitch, etc., that condenses in valve boxes and collector main. The liquor flows to a tar decanter where the tar is drawn off and the supernatant liquor is recirculated to the collector main again. Excess supernatant liquor from the decanter is pumped to the dephenolizing tower where phenols are removed by means of benzol extraction.

11. Primary Coolers

Gas from the collector main is drawn through a suction line to primary coolers where the gas is cooled to a temperature of 25° to 30° C. These

are indirect coolers with the flow of gas being counter current to the flow of cooling water through the cooling jackets. After passing through these units the discharged cooling water is utilized for coke quenching.

Water, tar, etc. condensed from the gases in these coolers are collected in the bottom of the gas chamber and flushed through a seal to the tar decanter where the tar is separated and the liquor recirculated to the flushing system of the collector main which receives the raw gases from the coke ovens. Any excess liquor is circulated to the dephenolizing tower.

12. Exhausters and Precipitators

The exhausters draw the gas from the primary coolers and force it through the remaining units of the system. Additional tar is removed from the gas by centrifugal force as the gas passes through these blowers. The tar collected in the bottom of the blowers is flushed through seals and returned to the tar decanter previously mentioned.

From the exhausters the gas passes to the Cottrell precipitators where the tar still remaining in the gas is separated. In these units the gas is passed through a strong electrical field produced by maintaining a high potential difference between two electrodes. The tar particles collect in the bottom of the precipitators and are flushed back to the tar decanter.

13. Phenol Recovery

The excess weak ammonia liquor from the tar decanter is treated in a dephenolizing unit before going to the ammonia still for ammonia recovery. In this unit the phenols are removed by the benzol extraction process. The unit consists of a scrubber 10 feet in diameter and 65 feet

in height with wood grids constructed from sawed wood slats. The benzol enters at bottom of scrubber through perforated pipe and flows countercurrently to the ammonia liquor which enters at the top through similar perforated pipe. The dephenolized weak liquor leaves the bottom of scrubber through an adjustable overflow and is discharged to a 150,000 gallon storage tank prior to going to the ammonia still. The phenolized benzol flows from the top of the scrubber to a caustic washer where the phenol is removed by a 20 per cent caustic solution. The dephenolized benzol is then returned to the scrubber and the cycle repeated.

The caustic washer, 12 feet in diameter and 60 feet high, is divided into four sections. The top section removes hydrogen sulfide, carbon dioxide, and other impurities from the benzol by means of a water wash. The benzol then flows through the next two sections, connected in series and containing 20 per cent caustic solution. When the solution in the number 1 washer is completely converted to sodium phenolate, it is removed and the solution from number 2 washer is transferred to number 1 washer. A fresh 20 per cent caustic solution is then placed in number 2 washer. The bottom or fourth section serves as storage or surge tank for the dephenolized benzol and from this section it is pumped back to the scrubber where the cycle is resumed.

The sodium phenolate removed from the caustic washers is passed through a centrifuge to remove any benzol, together with any neutral oils and naphthalene that may be in the phenolate. Following this the sodium phenolate is treated in an agitator with 66° Baume sulfuric acid. In this operation the crude phenol floats on the surface of the sodium sulfate solution formed. The crude phenol is drawn off to a storage tank while the sodium sulfate is drained to a recovery sump.

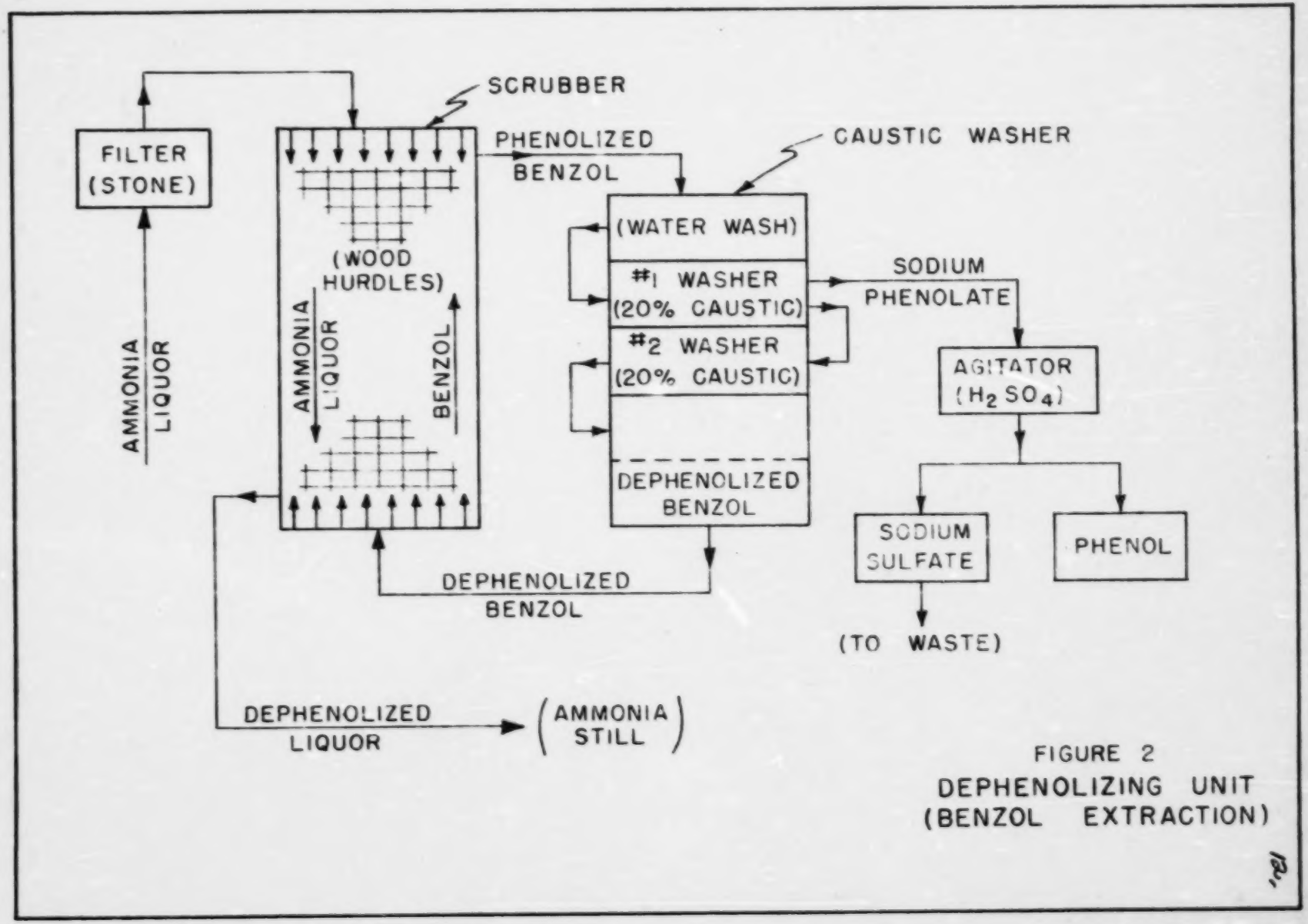


FIGURE 2
DEPHENOLIZING UNIT
(BENZOL EXTRACTION)

A flow diagram of this phenol recovery plant operation is shown in Fig. 2.

14. Ammonia Recovery

Surplus flushing liquor from the collector main and primary coolers, after passing through the tar decanter and dephenolizing tower, is passed to the ammonia still where ammonia is recovered by steam distillation. The ammonia vapors from this still are added to the gas from the Cottrell tar precipitators and then passed through the ammonia scrubber. The ammonia still consists of a fixed leg and a free leg through which the liquor flows in series. A reservoir containing milk of lime solution is located at the bottom of the free leg. Weak ammonia liquor entering the top of the free leg has the free-ammonium salts decomposed by the steam and the ammonia, hydrogen sulfide, carbon dioxide, and hydrogen cyanide driven off. As the liquor then passes through the milk of lime solution in the bottom of the free leg the fixed ammonium salts are decomposed and the ammonia freed in this way is distilled off when the liquor then passes to the fixed leg of the still. The waste liquor after passing through the still is discharged to a lime settling sump and from there to the sewer.

15. Ammonia Scrubbers

As previously mentioned the gas from the ammonia still is combined with the gas from the Cottrell precipitators and passed through the ammonia scrubbers. In this operation the gas passes up through the scrubbers and is intimately contacted with a weak solution of sulfuric acid sprayed into the top of the scrubber, forming ammonium sulfate mother liquor. The gas passes through a mist removing section in the top of the scrubber and then passes on to the final gas coolers at the benzol plant. The mother liquor produced in the scrubber is concentrated by evaporation until it precipita-

tes the ammonium sulfate crystals which are then water washed and dried suitable for the commercial trade.

16. Pyridine Production

In order to produce ammonium sulfate that is practically free of pyridine a pyridine recovery system is used to remove the pyridine bases from the mother liquor. The process consists of continuously withdrawing a portion of the mother liquor to a tank where it is neutralized with ammonia vapors from the fixed leg of the ammonia still. The mixture of neutralized liquor and pyridine bases is discharged to a separator where the pyridine separates and floats to the top and is withdrawn to storage. The mother liquor is withdrawn continuously from the bottom of the separator and returned to sulfate plant. A flow diagram of the recovery system is shown in Fig. 3.

17. Final Coolers

The gas discharged from the ammonia scrubbers is taken to a final cooler where the gas is cooled and naphthalene removed. This is a direct cooler containing wooden grids. The gas enters the bottom and flows upward while the cooling water enters at the top and flows down over the grids counter-currently to the flow of gas. The temperature of the gas is lowered about 25° to 30° C. passing through cooler, and leaves the cooler at a temperature of 20° to 30° C.

The cooling water containing considerable naphthalene in suspension, as it leaves the cooling tower, passes through naphthalene recovery sumps where the naphthalene floats to the surface and is skimmed off. After separation of the naphthalene the water is pumped to a Marley cooling tower where the temperature of the water is lowered before being returned to the final cooler where the cycle is resumed.

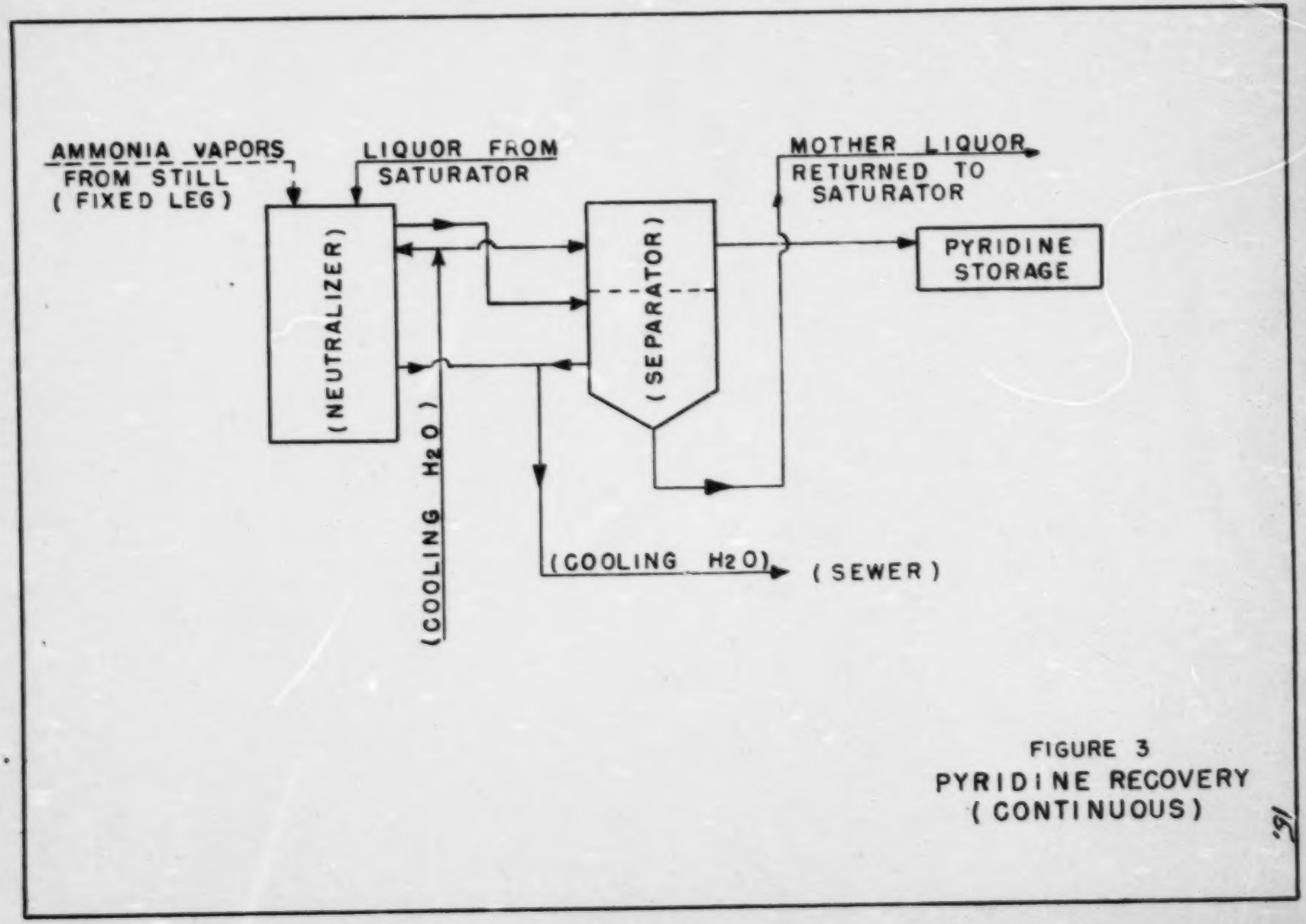


FIGURE 3
PYRIDINE RECOVERY
(CONTINUOUS)

91

18. Benzol Washers

After going through the final coolers the gas passes to the benzol washers or scrubbers where the light oil in the gas is removed or absorbed by scrubbing with a wash oil. This unit is a countercurrent scrubber where the gas is introduced at the bottom and flows upward and the wash oil is introduced at the top and flows downward over wood hurdles. Three of these scrubbers are operated in series at this plant. The wash oil used is a high boiling point oil. Benzene, toluene, and xylenes are the principal constituents of the gas which are absorbed by the wash oil. The benzolized or enriched wash oil from the scrubbers is then passed through a wash oil still in which the light oil is separated by direct steam distillation. The debenzolized wash oil is cooled in indirect coil coolers and returned to the scrubbers where the cycle is resumed. The cooling water used for one half of the wash oil coolers, which is river water, is discharged through an intercepting sump to the plant sewers. The balance of the wash oil cooling coils are cooled by water that is recirculated through an old cooling tower that had previously been used in the final cooler system. This part of the wash oil cooling system is a closed system in which the cooling water does not reach the sewers. The wash oil is also passed through a decanter where sludge and dirt are settled out and any water that condenses and separates is discharged to the plant sewers through the intercepting sump.

The gas discharged from the scrubbers, after the light oils are removed by absorption in the wash oil, is taken to the gas holder to be used for fuel in the coke ovens.

19. Light Oils and Their By-Products

The mixture of steam and light-oil vapor leaving the top of the wash-

oil still goes to a crude residue column where a preliminary fractionation into primary and secondary light oils takes place. The secondary phase consists of the higher boiling light-oil compounds, such as naphthalene, etc., which are separated and sent to the naphthalene still. Decanted water is discharged to the sewer through the intercepting sump.

The primary light-oils, after passing through decanters for removal of condensed water, go to an agitator where washing with 66° Be. sulfuric acid takes place. In this operation the sulfur-containing and unsaturated organic compounds are removed. The acid and impurities are separated and disposed of as a sludge in an open pit. The washed light-oils remaining after this acid treatment are neutralized with a 10% caustic solution. The spent caustic, which amounts to approximately 600 gal. per day, is discharged to the sewers through the intercepting sump.

The washed light oil or crude benzol from the agitator goes to a residue removal column. From this unit the residue is discharged to tar storage and the residue free oil is distilled in fractionating stills into pure products and intermediate fractions.

20. Tar Disposal

The characteristics of the tars recovered at different points in the plant vary to a great extent. The higher boiling point tars, or so-called heavy tars, are precipitated out of the coke oven gases in the collecting mains from the ovens. The tars recovered from the primary coolers, exhausters, and precipitators are largely lower boiling point compounds or so-called light tars.

The crude tar produced is sold on the market without any further processing or refinement at this plant.

SURVEY PROCEDURES

2. Sample Collection

During the period from May 14 to May 25 samples of the dephenolizing plant influent and effluent, and ammonia still effluent were collected by plant personnel. During the balance of the survey all sample collections were made by P. H. S. trailer laboratory personnel. Samples were collected at hourly intervals from 11:00 P.M. to 7:00 A.M., and composited.

Routine samples were collected at the following points:

(a) Plant intake water

(b) Influent - dephenolizing plant

(c) Effluent - dephenolizing plant

(d) Influent - ammonia still

(e) Effluent - ammonia still

(f) Influent (cooling water) - final coolers

(g) Effluent (cooling water) - final coolers

(h) Main intercepting sump (benzol plant)

(i) Wash oil cooler intercepting sump

Special samples were collected at several points in the light-oil treatment operations in the benzol plant, and also quench water samples from the coke quenching stations. Samples of the exhaust air from the Marley cooling tower were collected over a four day period for the purpose of tracing possible losses to the atmosphere of certain substances produced in the carbonization process.

The combined wastes discharged from the coke plant were not sampled due to the impracticability of segregating these samples from the overall steel plant wastes. The coke plant outfall connects into the main plant outfall at a junction manhole approximately 50 feet in depth. Personnel and equip-

ment available did not permit sample collection of the combined coke plant flow prior to its discharge to the steel plant wastes.

22. Flow Measurements

In some cases the volumes of water used in certain operations were metered and the quantities of liquid wastes were determined from the meter charts. The metered flows included the flows through the dephenolizing plant, ammonia still, and final cooling system. In some instances the flow figures were furnished by plant officials and were based on the service water charges against various departments of the plant. In the case of discharges from certain individual units such as decanter overflows in the benzol plant there were no data available on volumes of discharge and actual gaging was impractical without interfering with plant operations. However, all such waste discharges passed through the intercepting sumps where the total waste volume from the benzol plant was estimated.

Discharges from the benzol plant are discharged through two intercepting sumps. The main intercepting sump receives the flows from the light oil decanters, caustic wash from the acid agitators, wash oil decanter, etc. The second intercepting sump received the discharged cooling water from one battery of the wash oil cooling coils. The total service water consumption in the benzol plant averages 3.0 m.g.d. according to plant personnel, and the total discharge tothe sewer throughthe two intercepting sumps was assumed to be this amount.

The proportionate amount of the total discharge passing through each sump had to be estimated since the structural features of the sumps did not permit any satisfactory means of gaging flows. It was estimated by plant personnel that the flow through the main intercepting sump was approximately 0.5 m.g.d. The second sump which takes the flow from the wash oil cooling

units had therefore a flow of approximately 2.5 m.g.d. The main sump and the wash oil cooling water sump are designated as sumps #1 and #2, respectively on the flow diagram accompanying this report.

23. Laboratory Analyses

The following determinations were made on the majority of the samples collected:

Phenols
Cyanides
Thiocyanates
Thiosulfates
Ammonia
Sulfides
pH
Alkalinity
Chlorides

The procedures used in making the above analyses were, in general, those outlined in "Standard Methods of Water and Sewage Analysis," 9th Edition, (1). Modified procedures followed for the determination of phenols, cyanides, ammonia, and thiocyanates are given in the appendix of this report.

EXPLANATION OF LABORATORY ANALYSES

A brief discussion of the significance of the various laboratory determinations is given below for the purpose of aiding in the interpretation of the analytical results reported.

24. Phenols

The phenol results, as reported, represent the gross quantity of phenolic constituents such as phenols, cresols, etc. These substances are produced in a by-product coke plant from the pyrolysis of the coal.

These substances are objectionable in the case of water supplies due to taste and odor problems created. In certain concentrations a detrimental effect is produced on some forms of aquatic life. Concentrations of 0.002 to 0.005 parts per million phenols in the presence of chlorine will produce

chlorophenol (medicinal) tastes and odors in water, and a concentration of 0.1 part per million of phenol alone will produce a noticeable taste and odor of phenol. In connection with effects of phenols on aquatic life, it produces paralysis of the neuromuscular mechanisms and hemolyzes the blood in fish. The concentrations producing toxic effects varies with different species of fish. Ellis' report states that Alexander, Southgate, and Bascindale found that 0.4-0.6 ppm caused trout to overturn in approximately 8 hours (3).

25. Cyanides

The cyanide results, reported as CN, includes the various cyanide salts and also HCN. Cyanides are very toxic substances and even when present in low concentrations can be fatal to the higher forms of aquatic life. According to Ellis, concentrations of 0.1 to 0.3 ppm KCN will kill goldfish in hard water in 3 to 4 days (3).

26. Sulfur Compounds

The compounds containing sulfur which are found in the wastes from this type of plant include sulfides, thiosulfates, thiocyanates, etc. Among the more important compounds from the standpoint of stream pollution is hydrogen sulfide since it is readily oxidized and creates an immediate oxygen demand on the receiving stream. It has been reported that a concentration as low as 0.1 ppm is lethal to brook trout (4).

27. Ammonia

These results represent the free ammonia and ammonium salts, but do not include the albuminoid ammonia and organic nitrogen.

Ellis and Chipman (1936) in reporting on their experiments found that the pH is a large factor in regulating thetoxicity of ammonium compounds for aquatic animals. It was found that the toxicity of ammonium compounds increased 200 per cent or more when the pH ranged from 7.4 to 8.0. The

data from the experiments indicate that under average stream conditions with a pH value of 7.4 to 8.5, a concentration of 2.5 ppm of ammonia will be harmful to many of the common aquatic species (5).

28. pH Value

The pH value is a measure of the relative acidity or alkalinity of a water or waste, decreasing values below 7.0 indicating higher degrees of acidity and increasing values above 7.0 indicating higher degrees of alkalinity. It is a measure of intensity rather than a quantitative measure.

29. Alkalinity

The alkalinity of a water or waste is due to its content of carbonates, bicarbonates, and hydroxides of the alkali and alkaline-earth metals which include sodium, potassium, calcium, and magnesium. In most cases, calcium and magnesium account for the major part of the alkalinity. Occasionally a portion of the alkalinity may be due to borates, silicates, and phosphates. The alkalinity results are expressed in parts per million calcium carbonate ($CaCO_3$).

30. Chlorides

The chloride content of a water often has considerable significance from a sanitary standpoint. Chlorides in water, aside from originating from salt deposits or infiltration of sea water, may also be derived from sewage, oil field wastes, and industrial wastes. Therefore, the presence of a higher chloride content than would be normal for the natural waters of a region is a strong indication of contamination from other than natural sources.

DISCUSSION OF RESULTS

According to information from plant officials it was learned that operations at this coke plant are essentially constant during each 24 hour period. The amount of by-product and the characteristics of the wastes produced are affected principally by the quality of coal carbonized, coking time in ovens, coking temperatures, etc.

Analyses were made on the service water used in order to determine the quality of raw water introduced into the various plant units. Any significant quantities of constituents in the raw service water were taken into account in computing the net quantities of wastes produced in the different plant operations.

The following table (Table 1) presents the data on coal consumption and finished products produced during the period of the survey:

(1) 3.5% Moisture Basis
(2) 2.5% Moisture Basis

Preceding page blank

TABLE 1 - PRODUCTION DATA

Date 1950	Coal (1) Carbonised (Tons)	Coke (2) Produced (Tons)	Gas Production (1000 cu.ft.)	Light Oil (Gal.)	Ammonium Sulfate (Tons)	Tar Produced (Gal.)
May 14	6992	5420	82,690	18,878	58.38	34,960
May 15	6985	5511	80,250	14,668	62.86	34,925
May 16	6998	5443	81,410	19,594	64.73	34,990
May 17	7071	5498	82,440	19,799	74.24	34,648
May 21	6993	5431	80,570	19,580	70.62	34,965
May 23	6929	5360	81,170	19,401	58.55	35,338
May 24	6902	5367	78,750	13,114	63.84	35,200
May 25	6930	5376	79,980	18,018	55.09	35,343
May 31	6670	5246	75,920	18,009	61.03	46,023
June 1	6838	5370	79,050	18,463	67.01	34,874
June 2	6865	5357	78,060	18,536	47.02	35,011
June 4	6807	5322	74,690	17,698	66.02	34,716
June 5	6775	5314	76,680	18,292	61.31	35,230
June 6	6814	5356	79,870	18,398	64.05	34,751
June 7	6805	5343	77,860	18,374	48.65	34,705
June 8	6746	5283	76,470	16,865	47.22	29,682
June 12	6661	5196	76,200	17,985	31.97	29,974
June 13	6750	5259	79,210	14,175	34.76	29,700
June 14	6754	5259	78,870	18,236	24.65	29,718
June 15	6793	5230	77,410	17,662	31.58	29,889
June 18	6787	5278	78,480	19,004	87.21	29,863
June 19	6553	5198	77,410	18,348	81.25	30,144
June 20	6636	5161	80,170	17,254	88.25	29,862
Average	6828	5329	78,853	17,841	58.71	33,674

(Table 1 - Production Data)

(1) 3.5% Moisture Basis

(2) 2.5% Moisture Basis

Average Coking Temperature - 1900° F.

(Flue Temperature)- 2500° F.

(Wall Temperature)- 2000° F.

Average Coking Time - 17 hours, 14 min. (Wilputte ovens)

Average Coking Time - 15 hours, 36 min. (Koppers ovens)

The analytical results and the quantities of the various polluting substances are shown in tabular form in tables 2, 3, 4, and 5.

Table 2 - Summary of Laboratory Analyses

Table 3 - Average Concentration of Constituents

Table 4 - Gross Quantities of Significant Constituents Discharged from Plant Daily

Table 5 - Net Quantities of Significant Constituents Discharged from Plant Daily

Table 2 is a tabulation of the individual laboratory analyses on samples collected during the survey. Table 3 shows the average concentration of significant constituents of the wastes sampled while Table 4 shows the average daily quantity of these constituents discharged from the plant. Since the raw intake water contains significant quantities of some of these constituents, Table 5 is presented to show the net quantities of such constituents that are chargeable to the plant.

TABLE 2 - SUMMARY OF LABORATORY ANALYSES

Date	Source of Sample	Sample No.	Flow m.g.d.	Phenols ppm	Cyanide (CN) ppm	Thiocyanate (NH_4SCN) ppm	Free NH_3 (N) ppm	Fixed NH_3 as N ppm	Thiosulfate (S) ppm	Sulfide (H_2S) ppm	Alkalinity (MO) ppm	Alkalinity (Phenols) ppm	pH	Chloride ppm
	Raw Intake Water													
5/31	(Service Water)	25		0.014	<0.2	ND	8.42	0.39	1.44	**<0.01	86	-	7.3	-
6/1	"	31		0.002	<0.2	"	8.39	0.17	0.48	** 0.43	94	-	7.3	25.
6/2	"	36		0.010	<0.2	"	10.3	0.11	<0.16	**<0.04	87	-	7.3	13.
6/4	"	42		(Tr.)	<0.1	"	0.59	<0.01	<0.16	** 0.21	60	-	7.3	16.
6/5	"	48		<0.001	<0.1	"	0.83	0.24	<0.16	** 1.02	24	-	7.3	11.
6/6	"	54		0.010	<0.1	"	0.92	0.18	<0.16	** 0.21	68	-	7.3	14.
6/7	"	59		0.004	<0.1	"	3.01	0.18	<0.16	** 0.21	60	-	7.3	20.
6/8	"	64		(Tr.)	<0.1	"	8.33	0.20	<0.16	**<0.04	56	-	7.3	20.
6/12	"	69		0.006	<0.1	"	6.31	0.35	0.96	** 0.26	80	-	7.3	25.
6/13	"	74		-	<0.1	-	5.92	0.20	<0.16	** 0.13	67	-	7.3	-
6/14	"	79		<0.1	<0.1	ND	4.74	0.25	<0.16	** 0.13	74	-	7.3	-
6/15	"	85		-	<0.1	"	5.49	0.11	<0.16	** 0.13	75	-	7.3	-
	Average			<0.015	<0.1	ND	5.27	0.20	<0.36	** 0.23	69		7.3	18
5/14	Phenolised Liquor	1	0.0752	561	41.0	788	3276	-	357	53.3	2690	1260	8.9	-
5/15	"	4	0.1314	591	29.7	814	3231	-	375	49.7	2820	1490	9.1	-
5/16	"	7	0.1314	639	35.5	752	-	-	366	35.1	2700	1360	9.1	-
5/17	"	10	0.1589	658	37.4	663	3444	-	402	29.5	2690	1320	9.1	-
5/21	"	13	0.1440	525	35.6	681	3136	-	398	35.1	2800	1440	9.0	-
5/23	"	16	0.0983	586	31.1	720	2974	78.4	378	42.9	2520	1390	9.0	-
5/24	"	19	0.1001	614	37.8	720	3086	56.0	368	51.0	2690	1230	9.1	-
5/25	"	22	0.1225	600	37.1	677	3024	84.0	376	54.2	2760	1470	9.1	-
5/31	"	26	0.0929	466	45.3	490	2486	28.0	263	51.0	2800	1670	9.2	-
6/1	"	32	0.0872	453	37.0	560	2850	84.0	304	48.9	2570	1570	9.1	-
6/2	"	37	0.0925	497	34.6	676	3136	< 5.60	386	39.5	2600	1690	9.1	-
6/4	"	43	0.1429	398	41.8	592	2733	< 5.60	270	60.8	2670	1640	9.1	-
6/5	"	49	0.1396	410	43.1	741	3332	78.4	398	34.6	2150	1560	9.1	-
	Average		0.1167	545	37.5	680	3059	68.1	357	45.0	2620	1468	8.9-9.2	
	(Ammonia Still Inf.)													
5/14	Dephenolised Liquor	2	0.0742	59.3	31.9	754	3214	-	346	21.9	2790	1630	9.0	4810
5/15	"	5	0.1176	63.2	24.4	770	2884	-	383	9.99	2890	1760	9.1	4650
5/16	"	8	0.1245	44.4	24.2	694	-	-	347	15.9	2700	1550	9.2	5100
5/17	"	11	0.1226	50.5	33.3	702	3175	-	375	11.5	2760	1520	9.3	5280
5/21	"	14	0.1263	73.1	31.2	722	3134	-	374	11.7	2650	1390	9.0	5300
5/23	"	17	0.0724	115.	25.7	700	3030	95.2	384	12.8	2600	1390	9.1	4700
5/24	"	20	0.0860	124.	27.5	708	3002	44.8	384	20.8	2670	1310	9.2	4950
5/25	"	23	0.0972	118.	34.2	715	3114	50.4	350	16.2	2800	1490	9.1	4950
5/31	"	27	0.1157	63.3	33.5	520	2716	22.4	284	14.5	2780	1750	9.3	4060
6/1	"	33	0.0945	53.7	27.9	493	2688	28.0	282	18.5	2760	1680	9.1	-
6/2	"	38	0.1145	39.6	29.5	640	3074	39.2	370	12.1	2700	1790	9.1	4470
6/4	"	44	0.0911	33.6	33.1	617	2750	< 5.60	270	37.0	3170	1900	9.1	4200
6/5	"	50	0.1400	34.8	34.3	634	2951	33.6	309	26.8	2670	1700	9.1	4450
	Average		0.0966	67.1	30.0	666	2976	44.8	343	17.7	2765	1605	9.0-9.3	4743

TABLE 2 - RESULTS OF LABORATORY ANALYSES Cont'd - 2

Date	Source of Sample	Sample No.	Flow m.g.d.	Hrs. Operated	Phenols ppm	Cyanide (CN) ppm	Thiocyanate (NH_4SCN) ppm	Free NH_3 (N) ppm	Fixed NH_3 as N ppm	Thiosulfate (S) ppm	Sulfide (H_2S) ppm	Alkalinity (MO) ppm	Alkalinity (Phenol) ppm	pH	Chloride ppm	Bil. (ϕ) Factor
5/24	Ammonia	3	°0.1016	24	40.7	18.4	539	36.4	-	156	46.4	3990	3250	>12.2	3510	1.37
5/25	Still	6	°0.1789	24	42.0	9.79	494	158.	-	231	21.4	3530	[illegible]	>12.2	3170	1.47
5/26	Effluent	9	°0.2527	24	21.2	5.92	360	52.6	-	129	25.7	9050	[illegible]	>12.2	2510	2.03
5/27	"	12	°0.1630	24	30.6	12.1	497	48.7	-	247	28.4	7310	6460	>12.2	3380	1.33
5/28	"	15	°0.1591	24	42.4	13.1	533	43.1	10.6	225	27.4	10420	9430	>12.2	4280	1.28
5/29	"	18	°0.1071	13.75	74.6	9.01	488	53.5	15.1	269	15.7	1570	1480	>12.2	3880	1.48
5/30	"	21	°0.1333	17.5	68.1	9.50	452	15.2	14.4	256	17.2	9800	8250	>12.2	3200	1.55
5/25	"	24	°0.0525	7.25	60.2	11.7	526	83.7	40.0	162	42.9	4950	4260	>12.2	3520	1.41
5/31	"	28	°0.1492	24	35.8	10.1	361	33.0	9.07	122	42.7	4300	3630	>12.2	3150	1.29
6/2	"	39	°0.1523	22.2	20.8	12.3	435	29.1	8.40	216	30.8	3140	2840	>12.2	3350	1.33
6/4	"	45	°0.1257	16.25	19.6	7.8	426	41.3	8.06	198	26.4	5900	4900	>12.2	3050	1.38
6/5	"	51	°0.1834	24	19.5	11.0	437	129.	7.84	186	34.6	4870	4300	>12.2	3390	1.31
	Average		0.1461		39.3	15.3	462	60.3	14.2	198	29.3	5619	5031		3351	
5/31	Harley	29	3.3178		289	196	401	165	5.26	122	6.38	69	-	6.5	40	
6/1	Tower	34	3.3840		271	186	780	674	11.2	247	75.2	(1387)	-	(8.3)	60	
6/2	(Intake	40	3.3451		301	183	813	376	3.36	269	27.8	(261)	-	(7.4)	45	
6/4	Water)	46	3.3684		244	220	622	240	7.28	214	12.1	22	-	6.3	46	
6/5	"	52	3.3955		220	221	533	204	2.80	188	8.93	26	-	6.1	36	
6/6	"	55	3.3849		230	232	456	168	5.04	165	4.88	22	-	5.9	40	
6/7	"	60	3.3379		260	203	448	157	8.40	142	6.38	16	-	5.9	32	
6/8	"	65	3.3653		265	213	395	143	6.16	109	7.08	12	-	5.7	28	
6/12	"	70	3.3840		258	214	278	100	6.16	74.4	6.37	13	-	5.7	25	
	Average		3.3643		260	207	524	247	6.18	170	17.21	25.1		5.7-6.5	39	
5/31	Harley	30	3.3178		278	24.9	400	170	3.92	122	6.38	71	-	7.5	35	
6/1	Tower	35	3.3840		279	44.1	783	690	13.4	247	10.2	(1351)	137	(8.4)	50	
6/2	(Ballot	41	3.3451		261	31.2	781	376	(10.56)	273	10.4	(261)	-	(7.7)	45	
6/4	Water)	47	3.3684		241	41.4	618	246	5.04	194	14.5	30	-	6.5	38	
6/5	"	53	3.3955		218	34.2	538	204	3.36	192	7.01	27	-	6.4	36	
6/6	"	56	3.3849		228	32.2	458	170	3.36	160	4.25	22	-	6.5	36	
6/7	"	61	3.3379		252	30.5	451	157	5.04	142	4.04	18	-	6.4	33	
6/8	"	66	3.3653		257	33.6	383	142	2.24	117	4.25	14	-	6.3	28	
6/12	"	71	3.3840		264	35.7	276	98	4.48	74.4	1.28	15	-	6.3	25	
	Average		3.3643		254	34.2	515	299	5.10	169	6.92	28.1		6.3-7.5	37	

TABLE 2 - RESULT OF LABORATORY ANALYSES Cont'd - 3

Date	Source of Sample	Sample No.	Flow m.g.d.	Phenols ppm	Cyanide (CN) ppm	Thiocyanate (NH_4SCN) ppm	Free NH_3 (N) ppm	Fixed NH_3 as N ppm	Thiosulfate (S) ppm	Sulfide (H_2S) ppm	Alkalinity (CaO) ppm	Alkalinity (Phenol) ppm	pH	Chlorine ppm
6/18	Coke Quench Water	93	1.36	0.36	<0.1	ND	3.50	<0.03	<0.16	<0.04	77	-	7.7	-
6/19	(Old Sta.)	99	1.36	0.40	<0.1	"	5.20	0.08	<0.16	<0.04	100	-	7.5	-
	Average			0.38	<0.1	ND	4.35	0.05-	<0.16	<0.04	88		7.5-7.7	
6/18	Coke Quench Water	96	1.07	0.08	<0.1	ND	3.89	0.08	<0.16	0.13	75	4	8.4	-
6/19	(New Sta.)	100	1.07	0.12	<0.1	"	2.52	<0.01	<0.16	0.34	63	2	7.8	-
	Average			0.10	<0.1	ND	3.20	0.04	<0.16	0.23	69	3	7.8-8.4	-
	Average (Old & New)			(0.24)	(<0.1)	(ND)	(3.78)	(0.05-)	<0.16	(0.14-)	(79)		7.5-8.4	
							(COKING PLANT SAMPLES)							
			(Est.)											
6/13	Main Intercepting Pump	78	0.5	9.25	3.7	ND	6.83	0.56	3.84	0.76	64	-	?.?	-
6/16	"	83	0.5	8.7	3.14	"	5.97	0.41	2.88	0.77	65	-	7.3	-
6/18	"	89	0.5	10.3	2.66	"	6.76	0.17	3.68	2.13	68	-	7.5	-
6/20	"	104	0.5	8.7	2.52	4.19	10.4	0.27	4.32	2.17	71	-	7.5	-
	Average		(0.5)	(9.24)	(3.01)	(1.05)	(7.41)	(0.35)	(3.68)	(1.46)	(66)		7.3-7.7	
			(Est.)											
6/13	Wash Oil Cooler	77	2.5	<0.001	<0.1	ND	4.73	0.28	<0.23	<0.06	70	-	7.2	-
6/16	Intercepting Pump	82	2.5	<0.1	<0.1	ND	4.57	0.20	<0.16	<0.04	67	-	7.3	-
6/18	"	88	2.5	<0.02	<0.1	ND	4.48	0.10	<0.16	<0.04	74	-	7.3	-
6/20	"	103	2.5	0.08	<0.1	ND	7.03	0.11	<0.16	<0.04	78	-	7.3	-
	Average		(2.5)	<0.05	<0.1	ND	(5.15)	(0.17)	<0.18	<0.04	(72)		7.3-7.5	
6/16	Decanter (Water Phase)	80		5.0	228	ND	32.6	1.57	<0.32	61.5	132	-	7.7	-
6/18	"	86		5.6	146	ND	40.9	0.50	8.96	52.3	128	-	7.7	-
6/20	"	91		16.6	151	38.3	47.2	0.39	5.12	68.3	164	-	7.5	-
	Average			9.1	175		40.2	.82	4.81	60.7	138	-	7.5-7.7	

TABLE 2 - SUMMARY OF LABORATORY ANALYSES Cont'd - 4

Date	Source of Sample	Sample No.	Phenols ppm	Cyanide (CN) ppm	Thiocyanate (NH_4SCN) ppm	Free NH_3 (N) ppm	Fixed NH_3 as N ppm	Thiosulfate (S) ppm	Sulfide (H_2S) ppm	Alkalinity (NO) ppm	pH
					(BENZOL PLANT SAMPLES)						
6/13	Wash Oil Decanter	76	7.44	<0.1	ND	7.22	0.42	4.80	1.19	67	7.9
6/14	"	81	7.4	<0.1	"	5.33	0.25	5.76	<0.04	64	7.7
6/15	"	87	8.6	<0.2	"	6.38	0.17	6.40	0.34	60	7.3
	Average		7.8	<0.1		6.33	0.28	5.65	0.52	64	7.3-7.9
6/20	Decanter (Water Phase)	102	116.0	4.5	7.18	9.18	0.67	9.44	3.15	26	7.3
6/19	"	98	0.10	1.10	ND	24.7	0.08	<0.16	0.13	97	7.9

ND—(None detected).
**—Methylene Blue titrations showed no H_2S.
( )—Not used in computing averages.
* —Calculated flows.
(ϕ)—Dilution factor calculated from chloride determinations. Used for calculating ammonia still effluent flows.

Note: Method of reporting analytical data:
Cyanides as (CN)
Thiocyanates as (NH_4SCN)
Free NH_3 as (N)
Fixed NH_3 as (N)
Thiosulfates as (S)
Sulfides as (H_2S)

TABLE 3 - AVERAGE CONCENTRATION OF CONSTITUENTS

Source	Flow m g d	Phenols ppm	Cyanides as (CN) ppm	Thiocyanates as (NH_4SCN) ppm	Ammonia as (N) Free ppm	Ammonia as (N) Fixed ppm	Thiosulfates as (S) ppm	Sulfides as (H_2S) ppm
Intake Water		<0.015	<0.1	ND	5.3	0.2	<0.36	0.23
Phenol Removal Pl.-(Infl.)	0.117	545	37.5	680	3059	68.1	357	45.0
Phenol Removal Pl.-(Effl.)	0.097	67.1	30.0	666	2976	44.8	343	17.7
Ammonia Still - (Infl.)	0.097	67.1	30.0	666	2976	44.8	343	17.7
Ammonia Still - (Effl.)	0.146	39.3	15.3	462	60.3	14.2	198	29.3
Intercepting Sumps:								
Main Sump	0.50	9.2	3.0	1.05	7.5	0.35	3.7	1.5
Wash Oil Cooler Sump	2.5	<0.05	<0.1	ND	5.2	0.17	<0.18	<0.04
Quench Water:								
Old Sta.	1.36	0.38	<0.1	ND	4.35	0.05	<0.16	<0.04
New Sta.	1.07	0.10	<0.1	ND	3.20	0.04	<0.16	0.23

"ND" means "Not Determined"

TABLE 4 - GROSS QUANTITIES OF SIGNIFICANT CONSTITUENTS DISCHARGED FROM PLANT DAILY

Source	Flow m g d	Phenols lbs.	Cyanides as (CN) lbs.	Thiocyanates as(NH_4SCN) lbs.	Ammonia as (N) (Free) lbs.	Ammonia as (N) (Fixed) lbs.	Thiosulfates as (S) lbs.	Sulfides as (H_2S) lbs.
Ammonia Still Effl.	0.146	47.8	18.7	564.0	73.6	17.3	241.6	35.7
Main Sump (No.1)	0.5	38.3	12.5	4.4	31.2	1.5	15.4	6.2
Wash Oil Sump (No.2)	2.5	*(<1.0)	*(<2.0)	*(ND)	108.3	3.5	*(<3.7)	*(<0.8)
Quench Water	2.43	5.2	*(<2.0)	*(ND)	87.6	0.9	*(<3.2)	2.1
Total	5.576	91.3	31.2	568.0	300.7	23.2	257.0	44.0

(* Not used in computing total quantities)
("ND" means "Not Determined")

TABLE 5 - NET QUANTITIES OF SIGNIFICANT CONSTITUENTS DISCHARGED FROM PLANT DAILY

Source	Flow m g d	Phenols lbs.	Cyanides as (CN) lbs.	Thiocyanates as(NH_4SCN) lbs.	Ammonia as (N) (Free) lbs.	Ammonia as (N) (Fixed) lbs.	Thiosulfates as (S) lbs.	Sulfides as H_2S lbs.
Plant Discharge		91.3	31.2	568.0	300.7	23.2	257.0	44.0
Intake Water		*(<0.7)	*(<4.6)	*(ND)	246.0	9.3	*(<16.7)	10.7
Net Chargeable to Plant		91.3	31.2	568.0	54.7	13.9	257.0	33.3

(* Not used in computing net quantities)
("ND" means "Not Determined")

31. Discharge

The total overall plant discharge was not actually measured in the field since the location of the outfall sewer previously explained did not permit making flow gagings with the personnel and equipment available. However, discharges from the principal plant units containing significant wastes were determined. The sum of these discharges averaged approximately 5.58 m.g.d. during the period of the survey.

The influent flow to the ammonia still was metered and the average daily flows were determined from the meter flow charts. The discharges from the still were calculated by using a dilution factor based on the chloride concentrations of the influent and effluent flows of the still. The low average daily discharges on some days are explained by the fact that the still is periodically shut down for intervals of several hours at a time. This procedure is followed since the rate of operation of the still is governed by the operation of the pyridine recovery plant. This rate exceeds the rate of production of weak ammonia liquor so a 150,000 gallon storage tank has been installed ahead of the ammonia still for receiving the discharge from the dephenolizing tower. When the surplus storage of weak ammonia liquor has been depleted in this storage tank it is necessary to shut down the ammonia still to permit reserve storage of weak ammonia liquor to accumulate.

The discharge through the two intercepting sumps was estimated on the basis of the quantity of service water charged against the benzol plant or 3.0 m.g.d. It was not practical to gage the flow through the main intercepting sump due to design features and method of operation.

Plant officials estimated the flow through this unit to average approximately 0.5 m.g.d., and a daily average flow of 2.5 m.g.d. through the sump receiving the cooling water discharged from the wash oil cooling coils. All the discharge from the benzol plant passes through these two intercepting sumps. The major portion of the wastes from this plant are contained in the 0.5 m.g.d. discharged through the main intercepting sump. A breakdown of this flow into the individual discharges from the various units in the benzol plant was not made since it was not practical to gage the discharges from various decanters, etc., without interference with plant operations. No estimates of these flows were available from plant officials. However, a limited number of analyses were made on the discharges from various points in the benzol plant in order to give some indication of the concentration of certain constituents in the discharges from certain steps in the operations within the benzol plant.

The amount of quench water discharged to the sewer was calculated on the basis of 5,500 gallons of water being used per quench. It was estimated that 20% of the quench water used was lost in steam through the quench station stacks, and that the coke after quenching retained 2.5% moisture by weight. On this basis the calculated discharge to the sewers was 2.43 m.g.d. from all four quench stations.

32. Ammonia Still Effluent

It will be noted from Table 4 that the ammonia still effluent contained the greatest quantity of significant constituents of any of the wastes discharged from the principal sources contributing to the overall plant effluent. The flow from this unit was approximately 2.5% of the

total flow from the four principal sources of discharge to the sewers. The following tabulation shows the percentage of the total wastes that are contained in the ammonia still effluent (from Table 4):

Constituent		% in Ammonia Still Effluent
Phenols	-	52.3
Cyanides as (CN)	-	60.0
Thiocyanates as (NH_4SCN)	-	99.2
Ammonia (free) as (N)	-	24.5
Ammonia (fixed) as (N)	-	74.5
Thiosulfates as (S)	-	94.0
Sulfides as (H_2S)	-	81.2

33. Intercepting Sumps

The only constituent contained in wash oil sump (No.2 shown on Fig. 1) discharge that is of any significance is the quantity of ammonia. This discharge is strictly service water that has been used only for cooling purposes in an indirect cooling system. The quantity of ammonia in this discharge is accounted for by the concentration of this constituent in the raw service water used in this cooling system.

As shown in Table 4 significant wastes from the benzol plant are contained in the discharge through the main intercepting sump. (No.1 shown in Fig.1). Of special significance are the concentrations of phenols and cyanides which average 9.24 and 3.01 p.p.m. respectively or 38.3 and 12.5 lbs. per day. Sulfides averaged 1.46 p.p.m. or 6.2 lbs. per day. Thiocyanates and thiosulfates averaged 1.05 p.p.m. and 3.68 p.p.m. or 4.4 and 15.4 lbs. per day respectively. The ammonia content can be wholly or in part attributed to the ammonia present in the raw service water used

in the operations.

34. Quench Water

The coke quench water discharged to the sewers contained a minor portion of the total plant wastes. Phenols averaged 0.24 p.p.m. or a total of 5.2 lbs. discharged daily, while the concentration of sulfides averaged less than 0.14 p.p.m. or less than 2.1 lbs. daily discharge. The quantity of ammonia, which averaged 3.2 p.p.m. or 87.6 lbs. daily in the quench water discharged to the sewer, can be attributed to the ammonia content of the raw service water used in the coke quenching operation.

SUMMARY

The quantities of liquid wastes and significant constituents discharged from the principal units of the plant are summarized as follows:

35. Quantity of Liquid Wastes Discharged

The average daily discharge from the four principal sources contributing industrial waste constituents amounted to 5.58 m.g. distributed as follows:

Source	Amount	% of Total
Ammonia Still Effluent	0.146 m.g.d.	2.6
No. 1 Intercepting Sump	0.50 m.g.d.	9.0
No. 2 Intercepting Sump	2.50 m.g.d.	45.0
Quench Water	2.43 m.g.d.	43.4

36. Quantity of Significant Constituents

Total quantities of significant constituents discharged daily in the plant wastes were as follows:

Constituent	Total in Effluent	In Raw Service Water	Chargeable to Plant
Phenols	91.3 lbs./day	*(<0.7) lbs./day	91.3 lbs./day
Cyanides (as CN)	31.2 lbs./day	*(<4.6) lbs./day	31.2 lbs./day
Thiocyanates(as NH_4SCN)	568.0 lbs./day	*(ND)	568.0 lbs./day
Free Ammonia (as N)	300.7 lbs./day	246.0 lbs./day	54.7 lbs./day
Fixed Ammonia (as N)	23.2 lbs./day	9.3 lbs./day	13.9 lbs./day
Thiosulfates (as S)	257.0 lbs./day	*(<16.7) lbs./day	257.0 lbs./day
Sulfides (as H_2S)	44.0 lbs./day	10.7 lbs./day	33.3 lbs./day

(ND) - None detected.

* - Not used in computing net quantities chargeable to plant.

37. Unit Values

The unit quantities of liquid wastes and constituents per ton of coal carbonized are as follows:

Total wastes	816.6 gal.
Ammonia Still Waste	21.4 gal.
Benzol Plant Waste:	
(a) Intercepting Sump No.1	73.2 gal.
(b) Intercepting Sump No.2	366.0 gal.
Quench Water Waste	356.0 gal.
Phenols	0.013 lbs.
Cyanides (as CN)	0.005 lbs.
Thiocyanates (as NH_4SCN)	0.083 lbs.

Ammonia (as N)	0.007 lbs.
Thiosulfates (as S)	0.038 lbs.
Sulfides (as H_2S)	0.005 lbs.

38. Average Yield

The average yield of coke and by-products per ton of coal carbonized is as follows:

Coke	1,561 lbs.
Gas	11,548 cu. ft.
Light Oil	2.61 gal.
Ammonia Sulfate	17.2 lbs.
Tar	4.93 gal.

SPECIAL STUDIES

During the period of the survey a series of studies were made on the operation of individual plant units. The purpose of these studies was to determine the efficiencies and also the effect of certain operations on some of the constituents produced in the coking process.

39. Dephenolizing Tower

The operation of this unit was described under Item 13, Discussion of Process, and a flow diagram is illustrated in Fig. 2. The purpose of this study was to determine the efficiency of this unit (benzol extraction process) in the removal of phenols from weak ammonia liquor. Analyses were made on the influent and effluent during the period from May 14 to June 5. The analytical results are shown as follows:

TABLE 6 - DEPHENOLIZING PLANT - PER CENT PHENOL REMOVED

Date	Infl. ppm	Effl. ppm	% Removal
May 14	561	59.3	89.5
May 15	591	63.2	89.3
May 16	639	44.4	93.1
May 17	658	50.5	92.3
May 21	* 525	* 73.1	* 86.2
May 23	* 586	*115	* 80.4
May 24	* 614	*124	* 80.0
May 25	* 600	*118	* 80.3
May 31	* 466	* 63.3	* 86.3
June 1	453	53.7	88.2
June 2	497	39.6	92.0
June 4	392	33.6	91.5
June 5	410	34.8	91.5
Average	525	47.4	90.9

* Not used in computing averages.

It will be noted that a marked drop in removal efficiency occurs during the period of May 21 to 31. According to plant officials this was due to the fact that operating personnel failed to replace the spent caustic solution in the caustic washer during this period. In view of this situation it was felt that the inclusion of these data obtained during the period of May 21 to 31 in computing the phenol removal efficiency of the unit would not be justified. The average phenol removal during the balance of the period of the study was 90.9% with a maximum removal of 93.1% on May 16.

40. Final Cooler System

This is a closed system in which the cooling water used in the final gas coolers (direct cooler type) is circulated through a Marley cooling tower and then returned to the gas final coolers to complete the cycle. No chemicals are added to the circulating water in this installation for the removal of hydrogen sulfide in the gas final coolers. This study was undertaken for the purpose of determining, if possible, the extent to which certain substances produced in the coking process, particularly cyanides, were retained or converted into other substances in the system. It has been maintained that the circulating water for the gas final cooler may serve to retain or bottle up a considerable amount of the cyanides. The possibility of cyanides being released to the atmosphere by the exhaust air from the Marley cooling tower has been mentioned. The objective of this study was therefore to determine if, (1) there was a build-up or accumulation of cyanides in the circulating system, (2) a conversion of cyanides to other substances which build up in the system,

or (3) a release of cyanides to the atmosphere through the exhaust stacks of the Marley tower.

Samples of the influent and effluent water and the exhaust air at the Marley tower were collected and analyzed to determine the concentration of the various constituents. Sample collections were made during four different periods covering an interval of six days. Exhaust gas from the Marley exhaust stacks was sampled continuously during the sampling periods and passed through three "Fisher-Milligan" gas washing bottles connected in series. The first two contained a caustic solution while the third contained an acid solution. The volume of gas sampled was measured with a gas meter connected in the line. The velocity of exhaust gas leaving the Marley stacks was calculated from pitot tube readings that were taken at various points over the stack opening. The total volume of gas exhausted was then computed from these velocity determinations. Two of the three exhaust stacks were in operation during the period of tests. The quantity of circulating water passing through the Marley tower was obtained from meter readings.

The concentration and quantities of significant constituents in the circulating water and exhaust gases from the Marley tower are summarized in Tables 7 and 8 respectively, as follows:

TABLE 7 - CONCENTRATION OF SIGNIFICANT CONSTITUENTS IN FINAL COOLER SYSTEM (HARSHY TOWER)

Source of Sample	Date	Sampling Time	Flow m.g.d.	Air Vol. Sampled cu. ft.	Phenols ppm	Cyanide as (CN) ppm	Thiocyanate (NH_4SCN) ppm	Ammonia as (N) Free ppm	Ammonia as (N) Fixed ppm	Sulfide as (HgS) ppm	Thiosulfate as (S) ppm	pH	Alkalinity (CaO) ppm
Infl. to Harley Cooling Tower	June 6	11:00 PM-6:00 AM	3.3869	-	230	232	456	168	5.04	4.68	165	5.9	22
	June 7	" "	3.3379	-	260	203	441	157	3.40	6.38	142	5.9	14
	June 8	" "	3.3653	-	265	223	395	143	6.16	7.81	109	5.7	12
	June 12	" "	3.3840	-	258	214	278	100	6.16	6.37	74.4	5.7	13
Average			3.3685		253	215	392	142	6.46	6.11	122	5.7-5.9	15
Effl. from Harley Cooling Tower	June 6	11:00 PM-6:00 AM	3.3869	-	228	32.2	458	170	3.36	4.25	160	6.5	22
	June 7	" "	3.3379	-	262	30.5	431	157	5.04	4.04	142	6.4	28
	June 8	" "	3.3653	-	257	33.6	383	142	2.24	4.25	115	6.3	14
	June 12	" "	3.3840	-	264	35.7	276	98	4.48	1.28	74.4	6.3	15
Average			3.3685		253	33.0	382	142	3.78	3.45	123	6.3-6.5	17
			Total Air (1000 cu.ft.) per 24 hr.s										
Air Effl. from Harley Tower (2 Exhaust Stacks in Operation)	June 6	2:30 AM-6:30 AM	702,258	22.8	0.11 mg.	10.2. mg.	(NH)	0.30 mg.	0.29 mg.	0.64 mg.	2.40 mg.	-	-
	June 7	12:25 AM-5:15 AM	720,920	30.5	0.30 "	11.8 "	"	0.56 "	0.16 "	<0.09 "	10.60 "	-	-
	June 8	11:35 PM-4:55 AM	683,596	33.0	0.18 "	10.8 "	"	1.30 "	0.16 "	1.02 "	2.88 "	-	-
	June 12	11:20 PM-4:20 AM	715,569	27.0	0.14 "	8.4 "	"	0.80 "	0.42 "	<0.13 "	9.60 "	-	-
Average			705,584	28.3	0.18 "	10.3 "	"	0.74 "	0.26 "	<0.47 "	6.37 "	-	-

TABLE 8 - QUANTITIES OF SIGNIFICANT CONSTITUENTS IN FINAL COOLER SYSTEM (MARLEY TOWER) PER 24 HOURS

	Date	Flow M.G.	Air Volume (1000 cu.ft.) per 24 Hours	Phenols Lbs.	Cyanide as (CN) Lbs.	Thiocyanate as NH_4SCN Lbs.	Ammonia as (N) Free Lbs.	Ammonia as (N) Fixed Lbs.	Sulfide as(H_2S) Lbs.	Thiosulfate as (S) Lbs.
Infl. H_2O to Marley Cooling Tower	6/6	3.387	-	6,495	6,549	12,877	4,743	142	132	4,658
	6/7	3.338	-	7,234	5,645	12,269	4,369	234	177	3,951
	6/8	3.365	-	7,415	5,961	11,056	4,002	172	196	3,051
	6/12	3.384	-	7,264	6,026	7,825	2,815	172	179	2,096
Average		3.368		7,102	6,045	11,007	3,982	180	171	3,439
Effl. H_2O from Marley Cooling Tower	6/6	3.387	-	6,437	908	12,369	4,800	95	120	4,519
	6/7	3.338	-	7,288	848	11,990	4,369	140	112	3,951
	6/8	3.365	-	7,194	941	10,720	3,975	63	120	3,276
	6/12	3.384	-	7,433	1,003	7,769	2,758	126	36	2,096
Average		3.368		7,088	925	10,712	3,975	106	97	3,460
Air Effl. from Marley Cooling Tower (2 Exhaust Stacks in Operation)	6/6	-	702,258	7.48	693	*(ND)	20	20	43	163
	6/7	-	720,920	24.08	947	"	45	13	<7.2	851
	6/8	-	683,596	8.22	494	"	59	7	47	132
	6/12		715,564	8.18	491	"	47	25	<7.6	562
Average			705,584	12.0	656	(ND)	43	16	<26.2	427

*(ND) - None detected

A summary of the quantities of constituents contained in influent and effluent circulating water in the tower and the exhaust gas to the atmosphere are shown in Table 9 as follows:

TABLE 9 - AVERAGE QUANTITIES OF SIGNIFICANT CONSTITUENTS IN FINAL COOLER SYSTEM (MARLEY TOWER)

Constituent	Infl. Water to Marley Cooling Tower Lbs./24 Hrs.	Effl. Water from Marley Cooling Tower Lbs./24 Hrs.	Decrease in Marley Tower (Circulating Water) Lbs./24 Hrs.	Marley Tower Exhaust Air Lbs./24 Hrs.
	(1)	(2)	(3)	(4)
Phenol	7102	7088	14	12.0
Cyanide (CN)	6045	925	5120	656
Thiocyanate (as NH_4SCN)	11,007	10,712	295	(None Detected)
Free Ammonia (N)	3982	3975	7	43
Fixed Ammonia (N)	180	106	74	16
Sulfide (H_2S)	171	97	74	<26.2
Thiosulfate (S)	3439	3460	(+21)	427

Column 3 in Table 9 shows the decrease in quantity of the various constituents in the circulating water as it passes through the Marley tower; computed on a 24 hour basis. However, it will be noted that there is a slight increase in the case of the thiosulfate content. This represents an increase in concentration (ppm) of about 0.8% which is less than the degree of accuracy that can be expected in the analytical determinations. In view of this it does not appear that any significance can be attached to the indicated increase of 21 lbs. per day of thiosulfates.

Column (4) shows the quantities of constituents contained in the exhaust gas from the tower exhaust stacks in lbs. per 24 hours.

It will be noted from Table 9 that the most significant change occurring in the system is the decrease in cyanide content in the circulating system through the tower. On the basis of analytical results obtained during the tests a loss of 5,120 lbs. per 24 hours occurs in the circulating water as it passes through the tower while the quantity released to the exhaust gas amounts to 656 lbs. per 24 hours. This leaves 4,464 lbs. of cyanides per 24 hours unaccounted for. Although there was a significant concentration of thiocyanates in the circulating water (approximately an average of 380 to 390 ppm as shown in Table 7) there was a slight decrease in passing through the tower, and none were detected in the exhaust gas during the period of the test. It is assumed therefore that little or no cyanides were converted into thiocyanates. It will also be noted from Table 7 that the concentration (ppm) of cyanides in both the influent and effluent water circulated through the tower remained reasonably constant throughout the period of the test, and the per cent reduction in concentration remained

practically constant.

The analytical results pertaining to the other constituents determined in this series of tests do not account for the difference in the quantity of cyanides lost in the circulating water and the quantity discharged in the exhaust gas from the Marley tower. On account of the complexity and reactivity of cyanogen compounds there are several possibilities as to the reactions that may take place. It is possible that hydrolysis, decomposition of unstable compounds from the exhaust gas stream, etc., may take place, which would account for the cyanide loss indicated by the analyses made.

It appears that further study will be required to determine the reactions taking place and the various other constituents that may be produced in the system before the cyanide results obtained on this study can be clarified. Such a study may involve a considerable amount of research in the analysis of both the circulating water and the exhaust gases in the Marley tower. The scope of the analytical work which the present study permitted was limited to a large extent by the time and facilities available so that further investigation into the matter was not undertaken.

REFERENCES

1. "Standard Methods of Water and Sewage Analysis," 9th Edition, A. P. H. A.

2. U. S. Public Health Service, "Ohio River Pollution Survey - Supplements to Part II," H. D. 266, 78th Congress, 1st Session U. S. Government Printing Office, 1944, pp 1091-2.

3. Ellis, M. M., "Determination and Measurement of Stream Pollution," U. S. Department of Commerce, Bureau of Fisheries Bulletin No.22, U. S. Government Printing Office. 1937, p. 427.

4. Ibid, p. 424.

5. Ibid, p. 393.

APPENDIX

PROCEDURE FOR CYANIDE ANALYSIS

SPECIAL APPARATUS

1. Distillation Apparatus

   One liter Pyrex distilling flask, #3360, with Graham condensers or equivalent. Equipment must be all glass with ground glass joints.

Reagents and Solutions

1. Sodium hydroxide, 10% solution
2. Sodium hydroxide, 2% solution
3. Lead acetate, 5% solution
4. Tartaric acid, 15% solution
5. Methyl orange indicator - Std. Methods 9th Ed., page 249
6. p-aminodimethylbenzalrhodanine, 0.02% in acetone
7. Silver nitrate solution 0.001 N

   Dissolve 0.1699 gms $AgNO_3$ in 1 liter of chloride-free distilled water.

Procedure

1. Make a 200 ml. portion of the sample alkaline to phenolphthalein, using a spot plate and cautiously adding 10% NaOH solution to avoid gross excesses.
2. Add 10 ml. of 5% lead acetate solution and mix well.
3. Filter, using a fluted filter paper and save filtrate.
4. Take a 105 ml. portion of the filtrate or if appreciable quantities of NaOH have been required, take a sample which will correspond to 100 ml. of the original portion. Add 15% tartaric acid until sample is acid to methyl orange using a spot plate. Add an additional 1 ml. of tartaric acid solution and dilute to 500 ml.

5. Using the all glass distilling apparatus, distill over 50 ml., catching the distillate in a 100 ml. graduate containing 50 ml. or 2% NaOH. The delivery tube from the condenser should extend well below the surface of the liquid in the receiving vessel.
6. Add about 8-16 drops of p-dimethylaminobenzalrhodanine indicator per 100 ml. of sample and titrate with 0.001 N $AgNO_3$ until yellow color turns to light salmon color.
7. Run a blank in parallel with the sample in order to determine the sensitivity of the indicator.

(The same amount of indicator should be used for all titrations, depending upon the color perception of the operator).

Calculation:

1 ml. 0.001 N $AgNO_3$ = 0.052 mg. CN

$$\text{ppm cyanides as CN} = \frac{(\text{ml. of } 0.001 \text{ N } AgNO_3 - \text{ml for blank}) \times 0.052 \times 1000}{\text{ml of sample}}$$

Reference:

Ryan, J. A. and Culshaw, G. W.

Use of P-dimethylaminobenzalrhodanine as indicator for the volumetric determination of cyanide.

Analyst 69, p. 370-1, (1944)

DETERMINATION OF PHENOLS

BROMINATION PROCEDURE

I Preliminary Screening Procedure

1 - To 250 ml. of sample, add 2 ml. of 10% $CuSO_4$ solution and bring the pH of the mixture below 4.0 by the addition of 10% phosphoric acid solution. Put the mixture in an all glass distillation apparatus. Distill over approximately 200 ml. Halt the distillation, and allow the distilling flask to cool until boiling ceases. Add 50 ml. distilled water to the distilling flask. Resume the distillation and continue until a total of 250 ml. has been distilled over.

2 - Acidify the distillate with 1 ml. of 10% phosphoric acid solution and add 5 ml. of 10% $CuSO_4$ solution. Transfer the mixture to a separatory funnel containing 75 grams of fined grained sodium chloride. Make 3 serial extractions with C.P. chloroform. On the first extraction, shake the mixture until the salt has completely dissolved. Use 50 ml. of chloroform per extraction. Collect the chloroform extract, discarding the aqueous phase after the third extraction. Combine the chloroform extract. Extract the chloroform twice with 75 ml. portions of 0.1 N sodium hydroxide. Discard the extracted chloroform. Combine the alkaline extract and make it up to 250 ml. using a volumetric flask.

II Estimation of "Phenol"

The purified phenol solution is examined for phenol as described by R. D. Scott, Ind. Eng. Chem., Anal. Ed. 3, 63 (1931).

DETERMINATION OF PHENOLS

GIBBS

I Preliminary Screening Procedure

(Same as for Bromination)

II Gibbs Procedure as given in Standard Methods

THIOCYANATES IN GAS AMMONIA LIQUOR

The amount of thiocyanates in the condenser liquor from a coal gasworks will vary from 0.1 to 1.0%. The amount formed depends on the amount of oxygen in the crude gas entering the scrubbers, or whether the well liquor is circulated. The oxygen oxidizes some of the ammonium sulphide to thiosulphate and free sulphur; the latter is immediately dissolved by some of the unchanged ammonium sulfide to form polysulphide. The hydrogen cyanide in the gas stream absorbed by the liquor is converted into thiocyanate by the polysulphide. Under these conditions 90-98% of the hydrogen cyanide in the gas may be absorbed in the scrubbers and converted into ammonium thiocyanate. With normal working conditions the thiocyanate contents will be about 0.1-0.2% in the liquor. The amount of thiosulphate present will vary as the thiocyanate.

A portion of the gas liquor is shaken up with an excess of dry lead carbonate in a flask until all the sulphide has been removed from solution. Filter, and take 100 ml. of the filtrate, and acidify with dilute sulphuric acid. The acid should be added gradually to avoid the violent effervescence due to the ammonium carbonate in solution. Sodium bisulphite solution is added, followed by cupric sulphate in excess; the mixture is raised just to the boil. and left to stand 3-4 hours. The cuprous thiocyanate precipitate, which is frequently of a dark or black color, due to a small quantity of copper sulphide, is filtered and thoroughly washed. The washed precipitate is then boiled with an excess of sodium hydroxide and again filtered and washed. The filtrate, when cold, is acidified with dilute nitric acid, a few drops of ferric nitrate or sulphate added, and titrated with 0.1 N silver solution until the red color of the ferric thiocyanate just disappears. One ml. of the silver solution is equivalent to 0.00761 gram of ammonium thiocyanate. (pp 397-398) Chapter XVII.

<u>Cyanogen Compounds. Their Chemistry, Detection and Estimation</u>
By Herbert E. Williams (Second Edition
London - Edward Arnold & Co.)

PROCEDURE FOR AMMONIA ANALYSIS

Special Apparatus

1. Distillation apparatus.
   One liter Pyrex distilling flask, #3360, with Graham condensers, or equivalent. Equipment must be all glass with ground glass joints.

Reagents and Solutions

1. Sulfuric acid, 0.02 N
2. Sodium hydroxide, 0.02 N
3. Phosphate buffer, 0.50 N
   Dissolve 14.30 gms of KH_2PO_4 and 90.15 gms. K_2PO_4 in 1 liter of NH_3 free water.
4. Indicator, methyl red. Make up according to directions in Standard Methods, 9th Edition, page 249.
5. Sodium Hydroxide, 10 per cent
6. Phosphoric Acid, 10 per cent

Procedure

1. Steam out the all-glass distilling apparatus until free of ammonia.
2. Adjust the pH of a portion of the sample to approximately 7.4 using 10% NaOH or 10% H_3PO_4.
3. Place a 10 to 100 ml. aliquot of the sample in the distilling flask and add 25 ml. of the phosphate buffer in order to maintain a pH of 7.4 during the distillation.
4. Dilute the sample in the distilling flask to 300 ml. with NH_3 free water.

5. Distill about 200 ml. of the sample into a 500 ml. Erlenmeyer flask containing 25.0 ml. of the standard 0.02 N sulfuric acid and 3 drops of indicator. The delivery tube from the condenser must extend below the surface of the liquid in the receiving flask.
6. Titrate the distillate with standard 0.02 N caustic against a blank which has been run in the same manner as the sample.

Calculations

$$N/50\ H_2SO_4 = N/50\ NH_3 = N/50 \text{ nitrogen} = \frac{14.0 \text{ gm/l}}{50} \quad 0.28 \text{ mg/ml}$$

$$\frac{\text{Vol. of acid} \times 0.28 \times 1000}{\text{Vol. of sample}} = \text{p.p.m. } NH_3 \text{ as nitrogen}$$

Notes

1. Samples should be kept in completely filled glass stoppered bottles in order to exclude air. No chemical preservatives are added.
2. All glassware should be washed with NH_3 free water.
3. All reagents should be prepared with NH_3 free water.
4. If quantity of NH_3 in sample is small the determination may be run colorimetrically, using Nessler's reagent. (Standard Methods, page 65-66, 9th Edition).